Determination of Se, Pb, and Sb by atomic fluorescence spectrometry using a new flameless, dielectric barrier discharge atomizer

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Abstract

A flameless atomizer for atomic fluorescence spectrometry (AFS), based on an atmospheric pressure dielectric barrier discharge, has been developed for the atomization of hydride-forming elements, such as Se, Sb and Pb. The atomizer (8 mm o.d, 35 mm length) was operated at a power less than 50 W. The discharge was sustained with argon at the flow rate of 0.85 L min^{-1} after optimization. The characteristics of the atomizer and the effects of different parameters (power, gas flow rate, and KBH_4 concentration) are investigated. The most attractive feature of this atomizer is its low operation temperature (~ 52 °C, detected at the outlet of the atomizer by a thermocouple), allowing both the radiation source and the detector to be placed in close proximity with the atomizer. The analytical performance of the atomizer has been evaluated, and detection limits for Se, Sb and Pb obtained with the present technique were 0.08, 0.11 and 0.27 μg L^{-1}, respectively. The accuracy of the system was verified by the determination of Se, Sb and Pb in reference material of spinage GBW 10015. The concentrations of Se, Sb, and Pb determined by the present technique agreed well with the reference values (Se: 92 ± 24 mg kg^{-1}, Sb: 43 ± 14 mg kg^{-1}, Pb: 11.1 ± 0.9 mg kg^{-1}). This detector is very promising for field elements detection with portable AFS.
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1. Introduction

The determination of trace elements has received increasing attention in biological and environmental studies [1]. For example, it is important to monitor the release of toxic elements into the environment because they may have adverse effects on plants and animals, and may even enter into the human food chain eventually. In particular, there is an increasing need for determining parts-per-billion levels of antimony (Sb) [2], selenium (Se) [3], lead (Pb) [4], and arsenic (As) [5]. Many analytical methods have been established to achieve the determination of these elements for different research purposes. The hydride generation (HG) technique [6] coupled with atomic spectrometry has been proven to be extremely useful in this regard owing to its ability of pre-concentration and separation from the sample matrix. Hydride generation-atomic fluores-

cence spectrometry (HG-AFS) has been gaining popularity in the last two decades because of its high sensitivity, selectivity and simple configuration for analytical automation. The advantages of AFS over atomic absorption spectrometry (AAS), in terms of sensitivity, linear range and spectral interferences, have been demonstrated both theoretically [7,8] and experimentally [9,10]. It should be noted that the quenching of the fluorescence has also been reported [11].

The increasing interest in field analysis has encouraged the development of instruments providing laboratory level analytical performance in field portable systems [12–14]. AFS can be performed with simple instrumentation equipped with a non-dispersive optical system, which provides the possibility of developing portable AFS systems for elemental analysis. Effective field portable AFS for trace elemental analysis requires compact and rugged atomizer components compatible with the outside. The current investigations on the analytical utility of AFS have been performed with the hydrogen-air or hydrogen–oxygen–argon combustion flame quartz furnace

atomizer owing to its good sensitivity. However, the high temperature of the atomizer hinders instrumental miniaturization because both the radiation source and the detector have to be placed far away from the atomizer. In addition, the unenclosed nature of the flame presents an additional constraint for miniaturization.

Recently, due to the growing demand for miniaturized instruments, there is a significant interest in developing small size plasma as part of the detector [15–20]. Several plasma sources have been explored, including the microwave induced plasma(MIP) [21–23], the capacitively coupled plasma (CCP) [24], the inductively coupled plasma(ICP) [25], the glow discharge(GD) [26], and the dielectric barrier discharge(DBD) [27,28]. Microplasmas have many advantages: small size, low gas and power consumption, and the relatively low manufacturing cost. It is therefore attractive to couple a microplasma atomizer with HG-AFS for the miniaturization and development of total analysis system.

The DBD plasma is a common method to create a non-thermal microplasma [29]. It is characterized by small size, simplicity, low gas temperature, excellent dissociation capability for molecular species, and low cost for instrumentation and maintenance. In addition, DBD plasma can be sustained at fairly low power and at atmospheric pressure, making it a desirable source for the fabrication of an on-site, real-time miniaturized instrument. A few studies on the use of a DBD in analytical spectrometry have been reported recently. Niemax and coworkers [27,28] have explored a low pressure DBD in conjunction with diode laser atomic absorption spectrometry for the decomposition of chlorofluocarbons and detection of Cl and F. The DBD has also been investigated as a detector for gas chromatography by Gras et al. [30]. In our previous studies [31,32], a low temperature atomizer for AAS, based on the DBD, was proposed for hydride-forming elements detection. The results showed that DBD-AAS is a sensitive detector for As, Se, Sb and Sn. The low temperature and small size are desirable for miniaturization. However, this atomizer can not be used directly for AFS because of the different optical system between AFS and AAS. In the AAS, the radiation source,

atomizer and detector are placed collinearly, whereas the fluorescence is often detected perpendicular to the incident excitation light in AFS. Moreover, the radiation from the DBD plasma may produce significant background noise for non-dispersive AFS owing to argon emission in the plasma. These problems must be addressed before DBD can be coupled with AFS.

In the present study, a flameless atomizer based on DBD for AFS has been developed and applied to the detection of Se, Sb, and Pb. The DBD atomizer is operated at low temperature (~52 °C), which makes a compact instrument possible. In addition, the atomizer is simple, can be easily fabricated, and has low power consumption, which is also preferable for the miniaturization of the total analytical system. The influence of power and gas flow rates on its performance was studied. This system is proposed as a field portable technique for the analysis of hydride-forming elements.

2. Experimental

2.1. Instrument and conditions

The intermittent flow HG-AFS was employed in the present study. As shown in the flow diagram of the system (Fig. 1), covalent hydrides were produced by pumping the sample and potassium borohydride in 0.5% NaOH simultaneously into a mixing T with a two-channel peristaltic pump. The gaseous hydrides generated were separated from the liquid by a gas–liquid separator (GLS) and then the hydrides were transported by carrier gas to the DBD atomizer. The plasma atomization cell, described below, was positioned between the lamp and photomultiplier tube. High-intensity hollow cathode lamps (HCLs) (AS-7, pulsed, General Research Institute for Non-ferrous Metals, Beijing, China) were used as the radiation source. The radiation from the HCL was focused with a lens onto the outlet of the atomization cell for excitation. The shape of the focused image was circular with a diameter of about 6 mm. The observation height was set at 5 mm above the top of the DBD atomizer after optimization. The resultant fluorescence
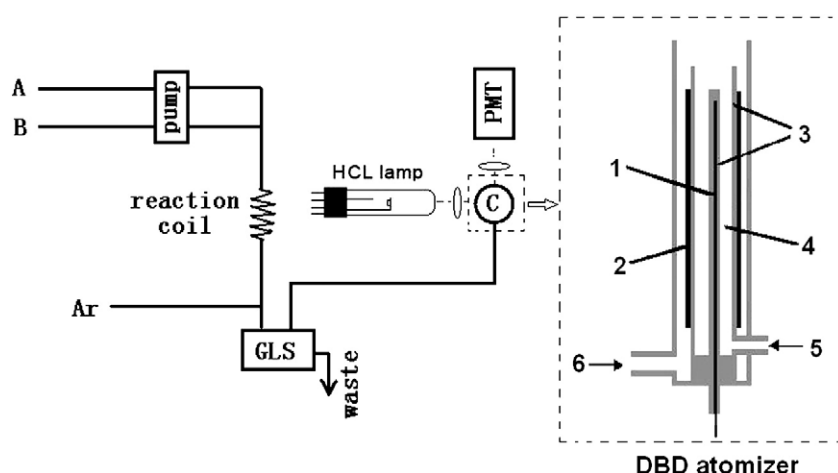

Fig. 1. The schematic diagram of the experiment setup (A: acidified sample or carrier solution; B: KBH_4 solution; C: atomizer; 1: high voltage electrode; 2: ground electrode; 3: quartz dielectric; 4: discharge gap; 5: carrier gas; 6: shield gas).

Table 1
Working program for the intermittent flow reactor

Step	Flow rate (mL min^{-1})		Time(s)	Function
1	Sample	3.1	10	Insertion of sampling tube into
	KBH$_4$ solution	1.7		sample solution
2	Sample	0	1	Change over of sampling tube
	KBH$_4$ solution	0		into carrier solution
3	Carrier solution	3.7	16	Readout
	KBH$_4$ solution	2.0		
4	Carrier solution	0	1	Return to step 1
	KBH$_4$ solution	0		

emission was detected at an angle of 90° with respect to the excitation beam using the photomultiplier tube. The working program of the intermittent reactor is described in Table 1.

In the present study, cylindrical configuration was employed for the DBD atomizer owing to its relative simplicity in construction. The atomizer consists of two concentric quartz tubes; the inner tube (4.0 mm i.d × 4.5 mm o.d) acts as the discharge reactor and the outer tube (7 mm i.d × 8 mm o.d) is used for a shield to prevent extraneous air from entering the plasma jet, and thus avoiding any reaction of gaseous atoms with ambient air. The DBD atomizer reactor consists of a copper wire a quartz tube, and an aluminum foil (Fig. 1). The copper wire and aluminum foil served as electrodes, while the quartz served as the dielectric barrier. AC high voltage (4.3–7.0 kV) was applied to the central Cu wire, and the outer electrode (Al foil) was maintained at ground potential for safety reason. The copper wire is embedded inside a quartz rode and placed in the center of the inner quartz tube in the DBD assembly. The gap length between the quartz rod and the inner surface of the quartz tube was 2 mm. Aluminum foil was wrapped around the outer surface of the quartz tube. The effective discharge length, dictated by the Al foil that wrapped on the outer surface of the quartz tube, is 20 mm. The gas temperature at the outlet of the DBD atomizer was measured by a thermoelectric couple at the power of 13.5 W. A home-made non-dispersive atomic fluorescence spectrometer was employed throughout this study. The operation conditions of the AFS are described in Table 2.

2.2. Reagents and samples

All the reagents were at least of analytical grade. Water was deionized and further purified with a Milli-Q water purification system (Millipore, Milford, MA). Stock solutions of 1000 mg L^{-1} of Se, Sb and Pb were purchased from the National Research Center for Certified Reference Materials of China and were stored at 4 °C in the dark. Working standard solutions of Se, Sb and their

Table 2
The operation parameters of HG-DBD-AFS

Parameters	Se	Sb	Pb
Lamp primary current (mA)	80	60	80
Lamp boost current (mA)	40	30	30
Flow rate of carrier gas (Ar) (L min^{-1})	0.8	0.8	0.8
Flow rate of shield gas (Ar) (L min^{-1})	1.3	1.3	1.3
Concentration of KBH$_4$ (m/v)	2%	2%	2%

mixtures were prepared daily by stepwise dilution of the stock solutions just before use. Lead working standard solutions were prepared daily by stepwise dilution of the stock solution with 1.0% (m/v) potassium ferricyanide (A.R., Shenyang Chemicals Co., Shenyang, China), and the acidity was adjusted to pH 5. The KBH$_4$ solution was prepared by dissolving KBH$_4$ (Tianjin Institute of Chemical Reagents, Tianjin, China) in 0.5% m/v NaOH (Beijing Chemicals Co.) solution. The standard reference materials, spinage GBW 10015 was obtained from the National Recearch Center for CRM's (NRCCRM).

3. Results and discussion

In the present work, the fluorescence is detected perpendicular to the incident light beam at the outlet of the atomizer. This design results from a number of considerations. It not only minimizes the background noise from the argon emission of the plasma, but also avoids the reflected radiation from the light source as found elsewhere [33]. In our primary studies, it was found that the sensitivity was poor without the use of a shield gas because of the reactions between the free atoms produced from the plasma and ambient air. Even with analyte concentration as high as 100 μg L^{-1}, the fluorescence intensity is very low if no shield gas is used. The signal intensity was improved by at least three orders of magnitude with the shield gas. Therefore, shield gas was employed in this work.

3.1. Optimization of operating parameters

To optimize the analytical fluorescence signal, the effect of discharge power and gas flow rate was evaluated. The potassium borohydride concentration was studied as the chemical parameters most affecting the production of hydride. Intermittent flow injection was used in the optimization with standard solutions of 10 μg L^{-1}. For the optimization studies, the peak area was used as the analytical parameter and three replicate injections were made for each experimental condition.
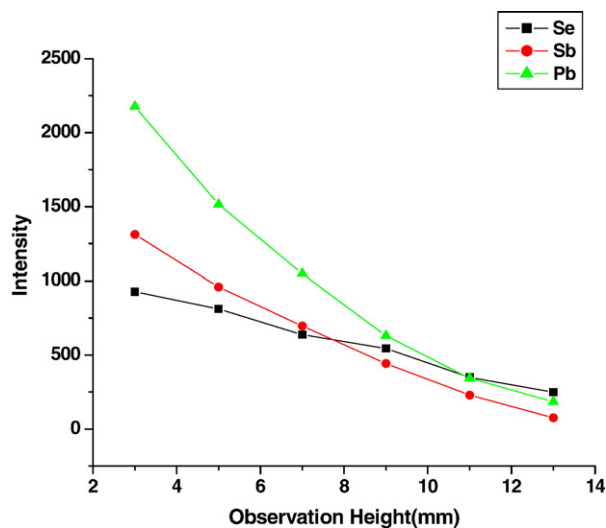

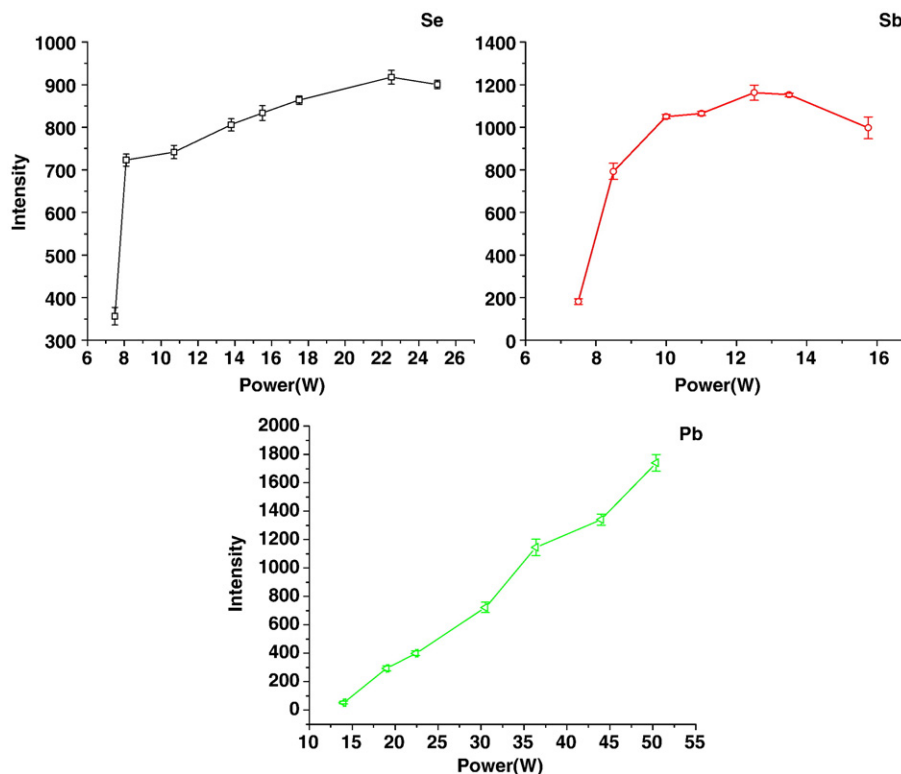Fig. 2. Optimization of the observation height.

Fig. 3. Optimization of discharge power on the fluorescence signal (Se, Sb, Pb).

3.1.1. Optimization of observation height

In the DBD atomizer, the hydride was atomized in the discharge zone and the fluorescence detected at the outlet of the atomizer. The observation height is an important factor for detection. Fig. 2 shows the effect of observation height on the fluorescence signal. It was observed that the signal decreased with increasing the observation height. It is not surprising since the free atoms react with air. However, at the observation height of 3 mm, the background intensity was higher due to the argon emission, producing lower signal/background ratios. Therefore, the observation height was set at 5 mm for best results.
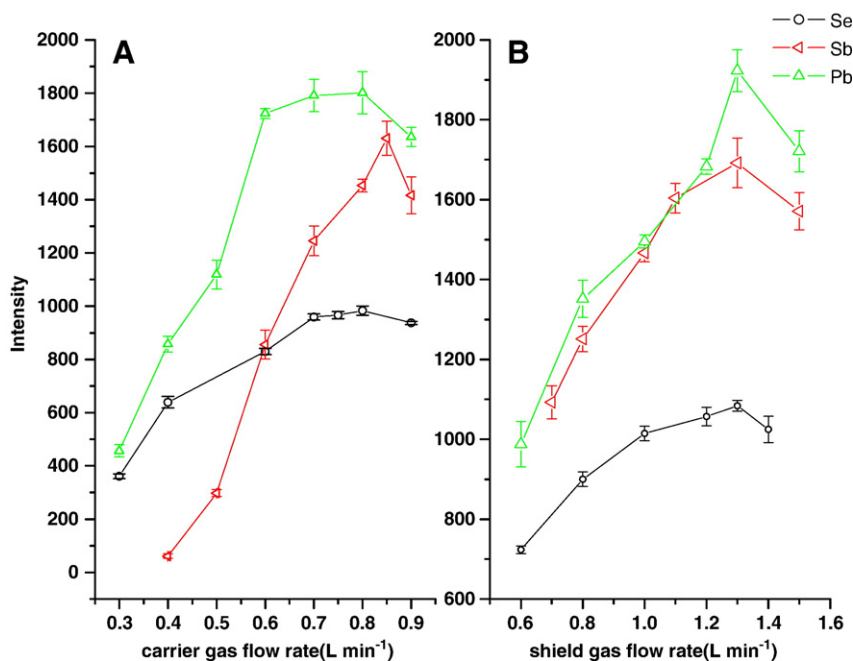

Fig. 4. The effect of gas flow rate on the fluorescence signal (A: carrier gas flow rate; B: shield gas flow rate).

3.1.2. Power

An Ar-DBD is generated as soon as power is applied to the electrodes. The plasma is light blue and fills the discharge tube. The plasma appears stable without any observable flicker or modulation. Fig. 3 shows the effect of the power on the fluorescence intensity of the hydrides was studied at an Ar flow rate of 0.6 L min^{-1}. Maximum fluorescence signals for Se and Sb were observed at the output power of 22.5 W and 12.5 W, respectively. The fluorescence signal decreased when output powers were set below 10 W. Increased power leads to a higher signal for Pb analysis. This result indicated that higher power produced higher atomization efficiency. However, high power induces instabilities in the discharge and also presents some potential problems for portable instrument. Therefore, power at 44 W was adopted for the detection of Pb in the remaining parts of the present study.

3.1.3. Gas flow rate

Argon was used in the present study owing to the lower fluorescence quenching and lower cost. The effect of Ar flow rate was investigated. Fig. 4 shows the fluorescence intensity dependence on the carrier gas flow rate. The maximum signal was obtained at a flow rate of 0.85 L min^{-1}. Signal decrease at higher flow rates, probably due to the dilution of the evolved volatile species and short residue of the analyte species in the atomizer. Therefore, an argon flow rate of 0.85 L min^{-1} was employed. In addition, an argon shield gas flow was employed to prevent extraneous air from entering the plasma jet, avoiding any reactions of gaseous atoms with air. Studies on the effect of the shield gas flow rate revealed that a flow at 1.3 L min^{-1} was optimal for yielding high signal intensities and improved signal-to-noise ratios. These results lead to the conclusion that an increase of the Ar flow rate result in a good inert gas atmosphere for the free atoms.

3.1.4. KBH$_4$ concentration

The KBH$_4$ concentration is a major factor that has a strong and definitive effect on the performance of HG. The effect of the
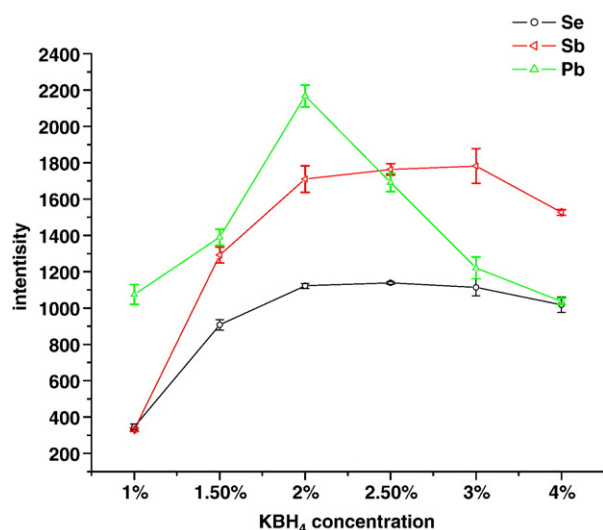

Fig. 5. Optimization of KBH$_4$ concentrations.

Table 3
Analytical performance of the proposed HG-DBD-AFS system

Elements	Linear range (µg L^{-1})	Relative coefficient	Limit of detection (µg L^{-1})
Se	1–400	0.9999	0.08
Sb	1–400	0.9992	0.11
Pb	1–400	0.9979	0.27

KBH$_4$ concentration was investigated from 1 to 4% w/v in a 0.5% NaOH medium. Fig. 5 shows the AFS signal variation versus potassium borohydride concentration. The results indicate that the signal goes up with increasing potassium borohydride concentration up to 2%. It can be concluded that the introduction of an increasing amount of H$_2$ to the discharge enhanced the atomization efficiency of hydrides as a result of the higher thermal conductivity of H$_2$ as compared to Ar and the relatively high dissociation temperature of H$_2$ [34]. However, the signals either remain constant or even decrease for further increase in KBH$_4$ concentration, probably due to a continuously increasing dilution of the analyte by the generated hydrogen and the reduced residue time of the analyte species in the atomizer. Therefore, a KBH$_4$ concentration of 2% was the optimum condition for the detection of Se, Sb, Pb.

3.2. Analytical performance

The analytical characteristic of the proposed procedure is given in Table 3. With the peak area as a quantitative parameter, the calibration graphs obtained were of very good linearity and wide linear ranges (1 to 400 µg L^{-1}). Repeatability, estimated from the relative standard deviation of the peak area was 1.6% ($n=11$) for the 10 µg L^{-1} Sb standard. The detection limits (DL) were evaluated based on three times the standard deviation (S. D.) of the blank signals ($n=11$). These results indicate that the proposed procedure has good sensitivity and repeatability.

3.3. Validation and sample analysis

To demonstrate the analytical accuracy of the present procedure, it was applied for the determination of total Se, Sb, and Pb in the CRM: GBW 10015 (spinage). The results of using a simple aqueous standard calibration technique are shown in Table 4; the determined concentrations of Se, Sb, and Pb are in good agreement with the certified values.

The developed procedure was also applied for the determination of total Pb and Sb in vegetables and total Se in human

Table 4
Analytical results (Means±s, $n=3$) of Se, Sb, and Pb in samples

Sample	Element	Certified value (mg kg^{-1})	Detected value (mg kg^{-1})	Recovery %
GBW 10015	Pb	11.1±0.9	11.0±0.2	97.6
	Se	92±24	87.8±2.8	93.5
	Sb	43±14	40.0±0.5	101.3
Human hair	Se		0.592±0.008	100.4
Zha Cai	Sb		0.030±0.003	96.8
Chinese Cabbage	Pb		0.180±0.001	99.5

hair. The analytical results are also included in Table 4. The samples were also spiked with a standard and a recovery factor was found to be close to 100%.

4. Conclusion

The atmospheric pressure DBD plasma described in this paper is a new flameless atomizer for atomic fluorescence spectrometry. It has been applied for the detection of Se, Sb, and Pb. The most attractive characteristic of the present DBD atomizer is the low operation temperature (~ 52 °C). This low operating temperature allows that the atomizer, the radiation source and the detector can be placed in close proximity. In comparison with other atomization techniques, the proposed technique has additional advantages: low power consumption, small size, simplicity of fabrication, and prevention of the contamination from the electrodes. The present atomizer exhibits good sensitivities for Se, Sb and Pb, which warrants further exploration of the application of the DBD. Moreover, it is possible to develop a DBD atomizer with a closed detection cell configuration, since the DBD atomizer did not use a H_2 flame to atomize the hydride. This not only facilitates the treatment of the residue poisonous hydride, but may also greatly reduce the gas consumption. In principle, fabrication of a miniaturized AFS employing this DBD atomizer is possible.

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